Thermochromic Excited – State Dipole Moment Measurements of p-Cyano-N,N-diethylaniline in Ethyl Acetate

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The effect of temperature on absorption and fluorescence spectra of p-cyano-N,N-diethylaniline (CDEA) in ethyl acetate has been studied for temperatures ranging from 293 K to 418 K. At T = 293 K two fluorescence bands are observed: long wavelength emission (LE) and short wavelength emission (SE) of much lower intensity compared to the first one. With temperature increase (which leads to the decrease of dielectric constant ε of the solvent) the intensity of SE band strongly increases, however its hypsochromic shift compared to the shift of LE band is rather slight. The electric dipole moments for CDEA determined based on this thermochromic method are: μ_e^{LE} = 13.4 D and μ_e^{SE} = 7.5 D for μ_g = 5.5 D, and μ_e^{LE} = 13.9 D and μ_e^{SE} = 8.3 D for μ_g = 6.6 D. The values obtained are compared with those of p-cyano-N,N-dimethylaniline (CDMA) determined using different methods.

Key words: Thermochromic Absorption and Fluorescence Band Shifts; Dipole Moments in the Excited State; Dual Fluorescence.

1. Introduction

Lippert and coworkers [1, 2] observed in 1961 that the fluorescence spectra of p-cyano-dimethylaniline (CDMA) and p-cyano-diethylaniline (CDEA) show a remarkable dependence on the solvent polarity. In nonpolar solvents only one emission band (SE) appears. With increasing solvent polarity the intensity of that band is reduced, and gradually the LE band (shifted to the red) gets more intensive. This second LE band is called the anomal fluorescence band.

Up to date the CDMA molecule has been thoroughly studied. Among others the electric dipole moments in the excited state have been determined using various methods, i.e., electrooptical, solvatochromic and thermochromic methods. The obtained results are significantly different.

In the current paper the electric dipole moments are determined for the CDEA molecule, differing from the CDMA by the alkyl group. Moreover, a discussion is performed on previously determined values of μ_e for CDMA.

For measurements of absorption and fluorescence of CDEA in ethyl acetate at different temperatures T, a high pressure cell described in [3 – 5] has been applied.

2. Results and Discussion

Based on the thermochromic shift of the absorption and fluorescence bands of CDEA in ethyl acetate, a hypsochromic shift of fluorescence with increase in temperature is observed, which is similar to the behaviour of CDMA in the same solvent [6], i. e., the fluorescence shift is strong for the LE band, but it is very weak for the SE band (Figure 1). This shift is caused by the diminishing permittivity ε and refractive index n with increasing temperature of the solvent.

The LE and SE spectra were recovered from the two overlapping component bands by a numerical simulation using the Gaussian distribution function (cp. [6]). However, the absorption band does not shift significantly between 253 and 418 K ($\Delta \tilde{\nu}_A \approx$ const). In this case, according to [6, 7], the value of the slope appearing in the equation for the shift of the absorption band $m_3 = (m_2 - m_1)/2$ is zero, which yields $m_1 = m_2$. In such a special case the shift of fluorescence band maximum, $\tilde{\nu}_F^{max}$, can be expressed as [6]

$$\tilde{\nu}_F^{max} = -m_2\,[f(\varepsilon,n) + g(n)] + \text{const}, \qquad (1)$$

$$\text{where } m_2 = 2(\mu_e^2 - \mu_g^2)/hca^3, \qquad (2)$$

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Table 1. Dipole moments (in Debye)*, in the lowest excited singlet state, determined from thermochromic shifts for CDEA and CDMA.

Molecule	Onsager radius a	μ_g	$\mu_\mathrm{e}^\mathrm{LE}$	$\mu_\mathrm{e}^\mathrm{SE}$	m_2^LE	m_2^SE
	Å	Debye			1kK = 10^3 cm^{-1}	
CDEA	5	5.5	13.4	7.5	12.0	2.1
CDMA	5	5.5	15.7	≈ 5.5	17.5	≈ 0

* The conversion factor for dipole moment: $[\mu]_\mathrm{SI}/Cm = 3.33564 \cdot 10^{-30}\,[\mu]_\mathrm{cgs}/D$, where D is the symbol for Debye and 1D = 10^{-18} esu · cm.

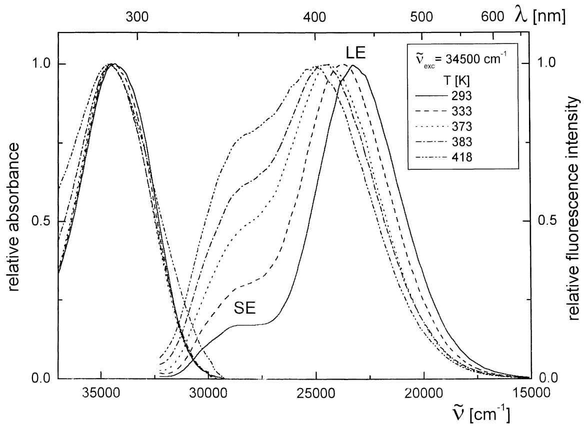

Fig. 1. Selected absorption and fluorescence spectra of CDEA in ethyl acetate at different temperatures between 293 K and 418 K.

$$f(\varepsilon,n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right), \qquad (3)$$

and

$$g(n) = \frac{3}{2}\frac{n^4-1}{(n^2+2)^2}. \qquad (4)$$

μ_g and μ_e in (2) denote electric dipole moments in the ground and excited state, respectively, a is the radius of the spherical Onsager cavity, h is Planck's constant and c is the velocity of light in vacuum. The permittivity ε and refractive index n have been determined from empirical formulas for $\varepsilon(T)$ and $n(T)$ for ethyl acetate [3].

Figure 2 shows the dependencies of maxima locations of the bands $\nu_\mathrm{F}^\mathrm{max}$ versus $f(\varepsilon,n)$ + $g(n)$ for both bands of CDEA, $\tilde{\nu}_\mathrm{F}^\mathrm{SE}$ and $\tilde{\nu}_\mathrm{F}^\mathrm{LE}$, and their description by (1). It can be seen that SE shifts very little, whereas LE shifts much. The coefficients m_2^SE and m_2^LE determined from respective slopes as well as the determined from (2) dipole moments, $\mu_\mathrm{e}^\mathrm{SE}$ and $\mu_\mathrm{e}^\mathrm{LE}$, together with μ_g [8] (the same as for CDMA in [6]) are listed in Table 1.

Table 2. Comparison of dipole moments in the excited state determined with different methods.

Molecule	Thermochromic Method			Electro- optical Methods		
	μ_g	$\mu_\mathrm{e}^\mathrm{LE}$	$\mu_\mathrm{e}^\mathrm{SE}$	μ_e		
	Debye					
CDEA	6.6	13.9	8.3	–	–	–
CDMA	6.6	16.0	≈ 6.6	12.5	12.8	14.9
				[9]	[10]	[11]

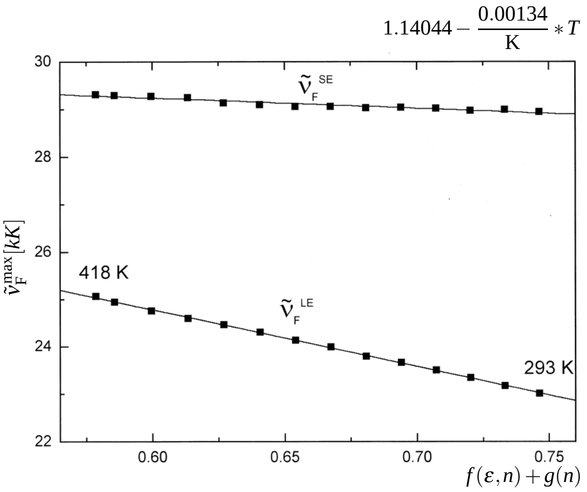

Fig. 2. Thermochromic shift of the fluorescence band $\tilde{\nu}_\mathrm{F}^\mathrm{LE}$ and $\tilde{\nu}_\mathrm{F}^\mathrm{SE}$ for CDEA in ethyl acetate according to (1).

For comparison, the same parameters obtained previously for CDMA can also be seen in this table. Table 2 contains, however, the values of μ_e obtained for CDMA using different methods, i. e., thermochromic and electro-optical methods. To make an appropriate comparison, the values of μ_e from Table 1 have been recalculated for μ_g = 6.6 D obtained by Czekalla et al. [9 – 11] and for the same value of a = 5 Å. The obtained values of μ_e = 16 D and 14.9 D given in Table 2 are close to one another and agree within the limit of experimental error. However, Suppan [12, 13] using a thermochromic method, obtained much higher values of μ_e (10 D for the $S_0 - S_1$ transition and 19.5 D for TICT) compared to our results listed in Table 1. The results obtained by Suppan can be questioned, since based on a few experimental points in a very narrow temperature range it is difficult to draw correct conclusions. Our thermochromic method differs from that of Suppan. We choose one solvent, i. e., ethyl acetate, and perform measurements changing the temperature every 10 K in a wide temperature range (in this case from 293 to 418 K, cp. Fig. 2). As a result we obtain the changes in ε and n according to the empirical formulas [3].

It should be underlined that for CDEA we obtained a small difference in the dipole moment $\Delta\mu^{\mathrm{SE}} = 2$ D (Table 1). The difference in the dipole moment $\Delta\mu^{\mathrm{LE}} = 7.9$ D is much greater than $\Delta\mu^{\mathrm{SE}}$, and the ratio of the charge displacements $\mu_{\mathrm{e}} - \mu_{\mathrm{g}}$ is for both cases approximately equal to 4.

Generally, it occurs that the obtained results do not confirm the conclusion drawn in [8] that the dipole moments of the excited states responsible for LE and SE are nearly identical.

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